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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :
C08B 31/12, D21H 17/29

A1

(11) International Publication Number: **WO 00/15669**

(43) International Publication Date: 23 March 2000 (23.03.00)

(21) International Application Number: PCT/FI99/00748

(22) International Filing Date: 14 September 1999 (14.09.99)

(30) Priority Data:
981991 15 September 1998 (15.09.98) FI

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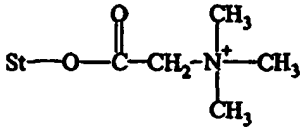
(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments
In English translation (filed in Finnish).

(54) Title: NEW CATIONIC STARCH, ITS PREPARATION AND USE



(I)

(57) Abstract

The object of the invention is a novel cationic starch which consists of natural products such as starch and betaine. In the product, betaine is covalently bound via an ester bond to a part of the hydroxyl groups of the starch, when the product has structural formula (I), wherein St represents the polymeric structure of the starch.

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NEW CATIONIC STARCH, IT'S PREPARATION AND USE

The object of this invention is a novel cationic starch, its preparation and use as an additive in the manufacture of paper.

Water-soluble cationic starches are used as an additive at the wet end in the manufacture of paper to increase i.a. the retention and improve the tensile strength of paper. The cationization of the starch is accomplished by processing starch with reagents having cationic groups. A cationizing reagent of this kind can contain cationic amino, immonium, ammonium, sulphonium or phosphonium groups, but nowadays industrially the most important cationic starches have been produced by etherifying a starch with compounds containing tertiary amino groups or quaternary ammonium groups. Among these, starches containing quaternary ammonium groups are the most popular, while they are, unlike the cationic starches containing amino groups, cationic under acidic, neutral as well as alkaline conditions. Quaternary starches are produced by forming ether or ester bonds between the hydroxyl groups of the starch structure and the cationizing reagent.

In addition to cationizing, the industrial cationic starches are also often modified by esterifying or etherifying the starch structure with short-chained carbohydrates, as well as by anionizing and cross-linking the cationic starch.

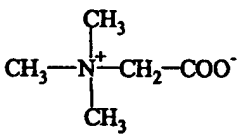
The first cationic starches used as a paper additive were patented in the US patent No. 2,813,093 in 1957, and since then cationic starches have been among the most common chemicals at the wet end in the manufacture of paper (cf. e.g. Modified Starches: Properties and Uses, Ed. O. B. Wurzburg, CRC Press, Boca Raton 1986). Cationic starches are still being developed for paper and other applications. At the moment, the cationic tertiary or quaternary aminoalkyl ethers of the starch are the most common additives in the manufacture of paper. In the manufacture of paper, by a small addition of a cationic starch mainly three advantages are achieved: the paper strength is increased and the amount of the fines in paper mill's white water is reduced, i.e. the binding of the

fines and pigments to the paper web is improved, and in addition to that, the water retention in the web is reduced. In textile industry, the textile feel of the web can be improved by using cationic starches, and in wastewater treatment the retention of the anionic impurities is increased in the flocculation processes.

Thus far, the starch has been cationized with compounds of petrochemical origin. Nowadays, efforts are made in finding more ecological solutions by saving non-renewable natural resources and utilizing renewable natural resources by indicating novel uses i.a. for the by-products of agricultural production. To fulfill this need, a novel cationized starch has now been invented which can be produced from natural products. The further advantage of the starch according to the invention is that it can excellently be applied to the cationizing necessary for foodstuffs and to paper and board used in foodstuff packages, because it is non-toxic, food grade and because betaine has useful nutritive properties.

In this invention, it is shown that a cationized starch can be produced by esterifying starch with betaine, ie. trimethyl glycine. The thus produced water-soluble cationic starch, ie. starch betaine, can be used as a food grade additive at the wet end in the manufacture of paper to improve i.a. retention, water permeability and the strength of the produced paper.

Betaine is an inner salt which contains a cationic quaternary trimethyl ammonium group. Betaine is a natural substance which is commonly found in wild plants, and sugar beet contains an especially large amount of it. Betaine is thus a natural and a renewable product, and as such it differs totally from the cationizing reagents of petrocemical origin known thus far which are very toxic. The structural formula of betaine is presented in the following figure.



The starch can be any natural starch, for example tuber-related starch (e.g. potato), root starch (e.g.. tapioca, arrowroot or sweet potato), or cereal starch (e.g. barley, wheat, rice or durra). In esterification, also waxy starches, modified starches, hydrolyzed or oxidized starches, acid-treated starches or even other long-chained polysaccharides can be used.

Starch esters, their production and properties as well as applications have already been known per se for decades, as they have been presented i.a. in the book Starch: Chemistry and Technology, 2nd Ed., edited by R. L. Whistler, J. N. BeMiller and E. F. Paschall, Academic Press Inc. 1984, and in the book Modified Starches: Properties and Uses, edited by O. B. Wurzburg, CRC Press, Boca Raton, 1986. Starch esters are used especially as plastics and their additives, in textiles and in the manufacture of paper, particularly for paper coating. Cationic starch esters have not been exemplified in the prior art literature, with some exceptions: the production of starch anthranil ester and its use as a paper retention aid has been described in the patent US 3,620,913 (1971), and the production of the reaction products of starch by using isatoic anhydride has been described in the patent publications NL 6,717,509 (1968), US 3,499,886 (1970), US 3,511,830 (1970), US 3,513,156 (1970) and US 3,620,913 (1970). Then anthranilate esters are formed containing primary amino groups which can be cationized, if desired, either at low pH or by alkylation with alkyl halides, sulphonates or other alkylation reagents. Respectively, the use of isatoic anhydride or quinolinic anhydride, i.e. 2,3-pyridinedicarboxyl acid anhydride, in the esterification of starch has been described in the patent US 3,052,561 (1962). The produced products are recommended to be used in the preparation of cationized starches. In the patent publication of Wacker-Chemie GmbH, DE 4,208,946 A1, the preparation of amino acid esters of starch is described, but the cationization of the products is not disclosed at all, and the products are mentioned to be applicable mainly to the focused needs of the medical industry.

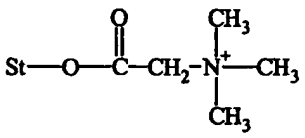
The use of betaine hydrazide for the derivatization of dialdehyde starch has earlier been described in the preparation of retention aids used in connection with the chemical pulp fibres (C. L. Mehltretter, T.E. Yeates, G. E. Hamerstrand, B. T. Hoffreiter and C. E.

Rist, *Tappi* 44, 1962, 750). However, the hydrazones of starch thus formed are toxic, their preparation is complex and the products are not natural at all.

In this invention, a natural amino acid, betaine, is used for cationizing starch. Thus a natural, strongly or weakly cationized starch, depending on the degree of substitution of the product, is obtained directly. The product is suitable for a retention agent in the manufacture of paper, for decreasing the water retention capacity of pulp and for increasing the strength of paper. The cationized starch described in this invention can preferably be used also for the purification of process water from fines for example in connection with the thermomechanical pulp preparation, as has been described by V. Bobacka, J. Näsman and D. Eklund in 1998 (*Journal of Pulp and Paper Science* **24**, 1998, 78). Due to its physiologically accepted properties, a betainyl ester of starch is applicable especially as an additive of food paper and food board and to effluent treatment.

Cationic starch betainate is produced by esterifying hydroxyl groups of starch with betainyl chloride or betainyl anhydride. The betainyl chloride used in the esterification is produced from anhydrous betaine, betaine hydrochloride or other inorganic or organic betaine salts. Betainyl chloride is an acid chloride which can easily be produced from betaine by known processes for the preparation of acid chloride. Betainyl chloride can preferably be produced from betaine by using i.a. tionyl chloride or oxalyl chloride in the presence of *N,N*-dimethyl formamide. Betainyl anhydride is in turn an acid anhydride, which is produced from betaine, betaine hydrochloride or other inorganic or organic betaine salts by water elimination (dehydration).

The structural formula of starch betainate is presented in the following. St represents the polymeric structure of the starch.



The esterification reaction is carried out in an organic solvent, preferably in 1,4-dioxan or toluene, by using a tertiary amine, preferably pyridine, as an esterification catalyte. The reaction is carried out at a quite high temperature, preferably near the reflux temperature of the used solvent. The reaction time is 1-24 h, preferably 2-6 h. In the following, an example of carrying out an esterification reaction is presented. When esterification is carried out by using betaine anhydride, the esterification can also be carried out in an alkaline water mixture.

The invention is illustrated in the following Examples.

Example 1

In this example a dry, native potato starch has been esterified. The esterification reaction was carried out in 1,4-dioxan, and pyridine was used as an esterification catalyte. In the laboratory scale, the procedure described in the following was used. The degree of substitution of the reaction product can be affected by reaction time, the amount of catalyte as well as the amount of the added betainyl chloride.

13 g of potato starch
19.8 ml (1 equiv.) of pyridine
13.9 g (0.33 equiv.) of betainyl chloride
156 ml of 1,4-dioxan

The starch was stirred in refluxing pyridine for 30 min. 156 ml of 1,4-dioxan and 13.9 g of betainyl chloride was added, and the reaction mixture was refluxed for 4 hours under argon at the temperature of 110°C. The solvent was poured from the reaction vessel, and the product was dissolved in water. The product was precipitated from water by adding ethanol, and the formed deposit was filtrated. The product was recovered, washed with a mixture of ethanol and diethyl ether and dried in vacuum. The yield was 14.3 g (63%) and the degree of substitution of the product was 0.9 (theoretical: 1.0).

Example 2

12 g of potato starch
18.3 ml (1 equiv.) of pyridine
9.5 g (0.25 equiv.) of betainyl chloride
150 ml of 1,4-dioxan

The starch was stirred in refluxing pyridine for 30 min. 150 ml of 1,4-dioxan and 9.5 g of betainyl chloride was added, and the reaction mixture was refluxed for 4 hours under argon at the temperature of 110°C. The solvent was poured from the reaction vessel, and the product was dissolved in water. The product was precipitated from water by adding ethanol, and the formed deposit was filtrated. The product was recovered, washed with a mixture of ethanol and diethyl ether and dried in vacuum. The yield was 11.83 g (60.6%) and the degree of substitution of the product was 0.39 (theoretical: 0.75).

Example 3

15 g of barley starch
23 ml (1 equiv.) of pyridine
14.3 g (0.3 equiv.) of betainyl chloride
200 ml of 1,4-dioxan

The barley starch was stirred in refluxing pyridine for 30 min. 200 ml of 1,4-dioxan and 14.3 g of betainyl chloride was added, and the reaction mixture was refluxed for 4 hours under argon at the temperature of 110°C. The solvent was poured from the reaction vessel, and the product was dissolved in water. The product was precipitated from water by adding ethanol, and the formed deposit was filtrated. The product was recovered, washed with a mixture of ethanol and diethyl ether and dried in vacuum. The yield was 16.15 g (61%) and the degree of substitution of the product was 0.07 (theoretical: 0.9).

Example 4

5 g of potato starch
7.6 ml (1 equiv.) of pyridine
6.3 g (0.4 equiv.) of betainyl chloride
60 ml of toluene

The starch was stirred in refluxing pyridine for 30 min. 60 ml of toluene and 6.3 g of betainyl chloride was added, and the reaction mixture was refluxed for 4 hours under argon at the temperature of 115°C. The solvent was poured from the reaction vessel, and the product was dissolved in water. The product was precipitated from water by adding ethanol, and the formed deposit was filtrated. The product was recovered, washed with ethanol and water and dried in vacuum. The yield was 1.12 g (11.2%).

Example 5

1 g of potato starch
15 ml of pyridine
0.18 equiv. of betainyl anhydride

The betaine anhydride was stirred in pyridine at room temperature. 1 g of potato starch was added, and the reaction mixture was heated to the temperature of 125°C. The reaction was allowed to continue for 6 h under argon at the temperature of 125°C. 100 ml of ethanol was poured to the reaction mixture, and the product was recovered by filtrating. The product was washed with a mixture of ethanol and diethyl ether. The yield was 1.54 g.

The produced cationic, water-soluble starch betainate is added to the wet end in the manufacture of paper 0.1-2% based on the amount of the chemical pulp fibre to improve the retention of fines and pigments, water permeability and the strength of the produced paper.

The cationized starch according to the invention can also be used as an auxiliary in textile industry and in the treatment of effluents, especially ligneous effluents, and in the waste reclamation.

In the following Table some examples of starch betainates produced in connection of the invention are presented.

Table 1. Starch betainates and the properties achieved by them.

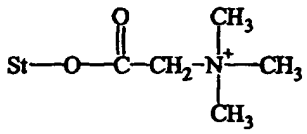
Sample	Starch content % based on the amount of the chemical pulp fibre	DS	Tearing strength index [a] (mNm^2g^{-1})	Tensile strength index [a] (Nmg^{-1})	Turbidity [b] (NTU)
No starch present	0	...	9.25	61.33	0.5
Starch betainate	0.6	0.44	9.95	67	0.3
Starch betainate	0.6	0.21	9.72	64.33	0.5
Starch betainate	0.6	0.06	8.8	60.83	0.4

a) The results were measured by SCAN-P 38:80 and SCAN-P 11:73 according to the standards by using 60 g/m^2 bleached birch-pine (60/40) paper sheets produced from sulphate pulp.

b) Bleached birch-pine (60/40) sulphate pulp was used in tests, and turbidities were measured by HACH 2100AN IS turbidimeter.

Claims

1. A novel cationic starch, **characterized** in that it consists of natural products such as starch and betaine and that in the product betaine is covalently bound via an ester bond to a part of the hydroxyl groups of the starch and that the product has the following structural formula, wherein St represents the polymeric structure of the starch.



2. A process for producing a novel cationic starch according to claim 1, **characterized** in that the cationic starch is produced by esterifying hydroxyl groups of the starch with betainyl chloride in an organic solvent by using a tertiary amine as an esterification catalyte.

3. A process for producing a novel cationic starch according to claim 1, **characterized** in that the cationic starch is produced by esterifying hydroxyl groups of the starch with betainyl anhydride in an alkaline water mixture or in an organic solvent by using a tertiary amine as an esterification catalyte.

4. The use of the cationic starch according to claim 1 or produced according to claims 2-3 as an additive in the manufacture of paper.

5. The use according to claim 4, **characterized** in that the novel cationic starch is used as an additive at the wet end in the manufacture of paper to improve the retention of fines, the dewatering properties of the paper web and the strength of the produced paper.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 99/00748

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08B 31/12, D21H 17/29
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08B, D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 3820030 C1 (TH. GOLDSCHMIDT AG), 27 July 1989 (27.07.89) --	1-3
A	US 4127563 A (JOHN C. RANKIN ET AL), 28 November 1978 (28.11.78) --	1-5
A	EP 0743394 A2 (NATIONAL STARCH AND CHEMICAL INVESTMENT), 7 May 1996 (07.05.96) --	1-5
A	US 3620913 A (STANLEY MARSHALL PARMERTER WHEATON), 16 November 1971 (16.11.71) --	1-5

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Information on patent family members

02/12/99

International application No.
PCT/FI 99/00748

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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